Exhibit 2

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(54) **ANTIREFLECTIVE COATING COMPOSITION, ANTIREFLECTION FILM, AND FABRICATION METHOD THEREOF**

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C08F 30/08 (2006.01)

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(58) **Field of Classification Search** 526/279; 528/41

See application file for complete search history.

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(57) **ABSTRACT**

An antireflective coating composition, antireflection films and fabrication method thereof. The antireflection film is constructed by stacked crosslink colloid particles, having a plurality of nanopores distributed uniformly therein. Due to the nanopores, the antireflection film has a refractive index less than 1.45, reducing the reflectivity of less than 3.0%. Furthermore, since the antireflection film comprises crosslink oxide colloid, the film exhibits superior mechanical strength and is suitable for use in display devices.

27 Claims, 4 Drawing Sheets

volume ratio exceeding 40%. The nanopores of the antireflection film are sufficiently filled by air, and the antireflection film exhibits refractive index less than 1.45, a reflectivity less than 3.0%, a transparency of more than 93%, a haze of 0.1~15%, and a pencil hardness exceeding F.

According to the invention, the method for fabricating antireflection film further comprises forming a protective layer on the antireflection film. The protective layer can be a hard coating used in display technology. Preferably, the protective layer comprises the condensation products of a compound with polymerizable groups having a formula (II):

$$_n(R^1)\text{—}M(OR^2)_m, \qquad \text{(II)}$$

and a compound having a formula (III):

$$_i(R^2)\text{—}M(OR^2)_j$$

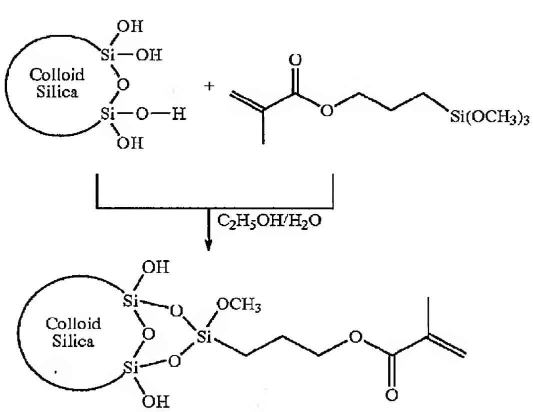
Accordingly, R^1 is alkenyl group, acrylic group, acryloyl group, epoxy group, or isocyanato group. R^2 is alkyl group or haloalkyl group. M is the same or different and Si, Al, Ti, Zr, Sn, or Sb. n and m are integers equal to or more than 1. i is an integer equal to or more than 0, and j an integer equal to or more than 1. The sum of i and j is an integer equal to or more than 2. The compound having a formula (III) can be tetramethoxysilane (TMOS), tetraethoxysilane (TEOS), methyl triethoxysilane (MTES), dimethyl dimethoxysilane, ethyl triethoxysilane, tetrapropoxysilane (TPOS), tetrabutoxysilane (TBOS), or combinations thereof.

The following examples are intended to demonstrate this invention more fully without limiting its scope, since numerous modifications and variations will be apparent to those skilled in the art.

Preparation of Polymerizable Oxide-Containing Colloid

Example 1

60 g of 3-methacrylicoxy-propyl trimethoxy silane (MPTS) and 140 g colloid silica (sold and manufactured under the trade number of MAST by Nissan Chemical Co., Ltd) with a diameter of 12 nm were dissolved in 1000 g H_2O/ethanol (H_2O:ethanol=1:1). After stirring for 4 hr at 70° C., a polymerizable colloid silica A was obtained. The reaction according to Example 1 is shown below.



Example 2

Example 2 was performed as Example 1 except for substitution of 80 g MPTS and 120 g colloid silica for 60 g MPTS and 140 g colloid silica, and a polymerizable colloid silica B was obtained. Particularly, the weight ratio between MPTS and colloid silica was 4:6.

Example 3

Example 3 was performed as Example 1 except for substitution of 100 g MPTS and 100 g colloid silica for 60 g MPTS and 140 g colloid silica, and a polymerizable colloid silica C was obtained. Particularly, the weight ratio between MPTS and colloid silica was 1:1.

Example 4

Example 4 was performed as Example 1 except for substitution of 120 g MPTS and 80 g colloid silica for 60 g MPTS and 140 g colloid silica, and a polymerizable colloid silica D was obtained. Particularly, the weight ratio between MPTS and colloid silica was 6:4.

Example 5

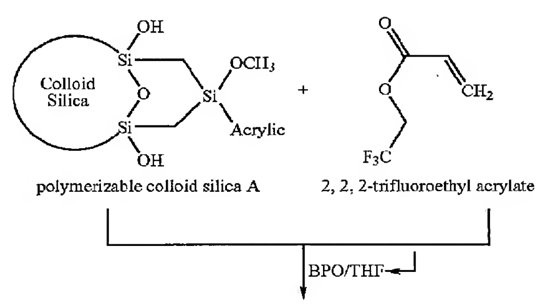
Example 5 was performed as Example 1 except for substitution of 140 g MPTS and 60 g colloid silica for 60 g MPTS and 140 g colloid silica, and a polymerizable colloid silica E was obtained. Particularly, the weight ratio between MPTS and colloid silica was 7:3.

Example 6

60 g of tetraethoxysilane (TEOS), 40 g colloid silica (sold and manufactured under the trade number of MAST by Nissan Chemical Co., Ltd) with a diameter of 12 nm, 0.4 g HCl, and 5 g 3-methacrylicoxy-propyl trimethoxy silane (MPTS) were dissolved in 1500 g ethanol and 250 g H2O. After stirring for 4 hr at 78° C., a polymerizable colloid silica F was obtained.

Example 7

60 g of polymerizable colloid silica A provided by Example 1, 140 g 2,2,2-trifluoroethyl acrylate, 0.75 g benzoyl peroxide (BPO) were dissolved in 100 ml THF. After stirring for 4 hr at 60° C., a polymerizable colloid silica G was obtained. The reaction according to Example 7 is shown below.



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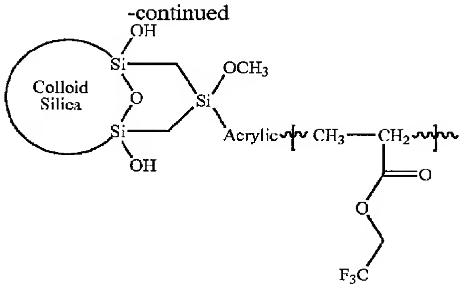

polymerizable colloid silica G

Example 8

Example 8 was performed as Example 7 except for substitution of 80 g polymerizable colloid silica A and 120 g 2,2,2-trifluoroethyl acrylate for 60 g polymerizable colloid silica A and 140 g 2,2,2-trifluoroethyl acrylate, and a polymerizable colloid silica H was obtained.

Example 9

Example 9 was performed as Example 7 except for substitution of 100 g polymerizable colloid silica A and 100 g 2,2,2-trifluoroethyl acrylate for 60 g polymerizable colloid silica A and 140 g 2,2,2-trifluoroethyl acrylate, and a polymerizable colloid silica I was obtained.

Example 10

Example 10 was performed as Example 7 except for substitution of 120 g polymerizable colloid silica A and 80 g 2,2,2-trifluoroethyl acrylate for 60 g polymerizable colloid silica A and 140 g 2,2,2-trifluoroethyl acrylate, and a polymerizable colloid silica J was obtained.

Example 11

Example 11 was performed as Example 7 except for substitution of 140 g polymerizable colloid silica A and 60 g 2,2,2-trifluoroethyl acrylate for 60 g polymerizable colloid silica A and 140 g 2,2,2-trifluoroethyl acrylate, and a polymerizable colloid silica K was obtained.

Preparation of Antireflective Coating Compositions

Example 12

10 g of polymerizable colloid silica A provided by Example 1, and 0.02 g triphenyl triflate were dissolved in 30 ml THF. After stirring completely, an antireflective coating composition A was obtained.

Example 13

10 g of polymerizable colloid silica G provided by Example 7, and 0.02 g triphenyl triflate were dissolved in 56.6 ml THF. After stirring completely, an antireflective coating composition B was obtained.

Example 14

100 g of polymerizable colloid silica A provided by Example 1, 6.6 g nematic liquid crystal (sold and manufactured under the trade number of E7 by Merck Co., Ltd) as a template, and 0.02 g triphenyl triflate were dissolved in 425 ml THF. After stirring completely, an antireflective coating composition C was obtained.

Example 14

100 g of polymerizable colloid silica A provided by Example 1, 6.6 g nematic liquid crystal (sold and manufactured under the trade number of E7 by Merck Co., Ltd) as a template, and 0.02 g triphenyl triflate were dissolved in 425 ml THF. After stirring completely, an antireflective coating composition C was obtained.

Example 15

100 g of polymerizable colloid silica A provided by Example 1, 6.6 g poly-ethylene glycol (PEG) as a template, and 0.02 g triphenyl triflate were dissolved in 425 ml THF. After stirring completely, an antireflective coating composition D was obtained.

Example 16

7 g of polymerizable colloid silica G provided by Example 7, 3 g pentaerythritol triacrylate, and 0.033 g triphenyl triflate were dissolved in 56.6 ml THF. After stirring completely, an antireflective coating composition E was obtained.

Example 17

5 g of polymerizable colloid silica A provided by Example 1, 1 g pentaerythritol triacrylate, and 0.02 g triphenyl triflate were dissolved in 30 ml THF. After stirring completely, an antireflective coating composition F was obtained.

Example 18

5 g of polymerizable colloid silica F provided by Example 6, and 0.02 g triphenyl triflate were dissolved in 3.5 ml ethanol. After stirring completely, an antireflective coating composition G was obtained.

Comparative Example 1

100 g of colloid silica (sold and manufactured under the trade number of MAST by Nissan Chemical Co., Ltd) was dissolved in 600 ml THF. After stirring completely, an antireflective coating composition H was obtained.

Preparation of Antireflection Films

Example 19

The antireflective coating composition A was coated on a glass substrate having a hard coating with a refractive index of 1.69 by spin coating at a speed of 2500 rpm for 30 sec. Next, the substrate was baked at 60° C. for 3 min and exposed to a UV ray, and an antireflection film A, with a thickness of 150 nm, was formed by polymerization of the antireflective coating composition A.

Afterward, the reflectivity and transparency of the antireflection film A were measured at a measured wavelength of 400~700 nm, as shown in FIGS. 4 and 5.

Example 20

The antireflective coating composition C was coated on a glass substrate having a hard coating with a refractive index of

1.69 by spin coating at a speed of 2500 rpm for 30 sec. Next, the substrate was baked at 60° C. for 3 min and exposed to a UV ray, and a dry film A was formed by polymerization of the antireflective coating composition C. Next, the dry film was immersed in acetone to dissolve the nematic liquid crystal, leaving an antireflection film B with a thickness of 100 nm.

Example 21

3-methacrylicoxy propyl trimethoxy silane (MPTS), tetramethoxy silane (TMOS), hydrochloric acid (HCl), and de-ion water (H2O) were put into a bottle and dissolved in ethanol at 60° C., with mole ratio of MPTS, TMOS, HCl, H2O, and ethanol is 0.25/0.75/0.1/4/15. After stirring for 3 hr, a hard coating composition A was obtained.

Next, the hard coating composition A was coated on the antireflection film B provided by Example 20. After heating at 120° C. for 3 hr, an antireflection film C, comprising the antireflection film B with a protective layer (10 nm) formed thereon, was obtained.

Example 22

The antireflective coating composition B was coated on a glass substrate having a hard coating with a refractive index of 1.69 by spin coating at a speed of 2500 rpm for 30 sec. Next, the substrate was baked at 60° C. for 3 min and exposed to a UV ray. After heating at 80° C. for 30 min, an antireflection film D, with a thickness of 100 nm, was formed.

Example 23

The antireflective coating composition G was coated on a glass substrate having a hard coating with a refractive index of 1.69 by spin coating at a speed of 2500 rpm for 30 sec. Next, the substrate was baked at 60° C. for 3 min and exposed to a UV ray. After heating at 80° C. for 30 min, an antireflection film E with a thickness of 100 nm was formed, and the profile thereof was identified by scanning electron microscopy (SEM) as shown in FIG. 6.

Example 24

30 g tetraethoxysilane (TEOS), colloid silica (sold and manufactured under the trade number of Snowtex-UP by Nissan Chemical Co., Ltd) with a diameter of 40~100 nm, and 0.4 g HCl were dissolved in 500 g ethanol and 250 g H2O. After stirring for 4 hr at 78° C., 3.0 g poly-ethylene glycol (PEG) was added into the mixture, preparing an antireflective coating composition.

The antireflective coating composition was coated on a glass substrate having a hard coating with a refractive index of 1.69 by spin coating at a speed of 2500 rpm for 30 sec. Next, the substrate was baked at 60° C. for 3 min and exposed to a UV ray. After heating at 80° C. for 30 min, a dry film was formed. Next, the dry film was immersed in acetone to dissolve the nematic liquid crystal, leaving an antireflection film F with a thickness of 100 nm.

COMPARATIVE Example 2

The antireflective coating composition H provided by Comparative Example 1 was coated on a glass substrate having a hard coating with a refractive index of 1.69 by spin coating at a speed of 2500 rpm for 30 sec. Next, the substrate was baked at 60° C. for 3 min, and an antireflection film G with a thickness of 150 nm was formed.

The hardness, adhesion, solvent-resistance, and haze of antireflection films B-G were measured. The surface hardness of the nanoporous film was measured through a pencil hardness test conforming to Japan Industrial Standard (JIS) K5600. The adhesion between the substrate and the nanoprous film was estimated by means of the cross-cut test conforming to JIS-K6801 (the symbol "⊚" indicates that all the films remained totally on the substrate; "X" indicates that at least one film was peeled off). The solvent resistance was estimated by dripping ethanol on the nanoporous film, and the change in appearance was observed (the symbol "⊚" indicates that the films were completely unscathed; the symbol "X" indicates that the film was damaged or eroded by ethanol). The haze of the nanoporous film was measured by hazemeter (MODEL TC-HIII, a product of TOKYO DENSYOKU Co., Ltd). The refractive index and reflectivity of the antireflection films were measured by MPC-3100 and UV-3150 spectrophotometer (manufactured by Shimadzu Corporation). The result is shown in Table 1.

TABLE 1

	Example 20	Example 21	Example 22	Example 23	Example 24	Comparative Example 2
hardness	3H	H	4H	2H	H	6B
adhesion	⊚	⊚	⊚	⊚	⊚	X
solvent resistance	⊚	⊚	⊚	⊚	⊚	⊚
haze (%)	0.9%	1.2%	1.0%	0.8%	0.8%	0.5%
refractive index	1.41	1.37	1.43	1.40	1.37	1.41
reflectivity	2.1	1.5	2.5	1.7	1.5	2.1

The antireflection film according to the present invention has a plurality of uniformly distributed nanopores. Due to the nanopores, the antireflection film has a refractive index less than 1.45, reducing the reflectivity of less than 3.0%. Accordingly, the antireflection film has a pencil hardness exceeding F, and a haze of 0.5~1.5%. Compared to conventional non-crosslink antireflection films (disclosed in Comparative Example 2), the antireflection film comprises of polymerizing colloid silica with a high crosslink density and exhibits superior mechanical strength and scratch resistance, suitable for use in display device.

While the invention has been described by way of example and in terms of preferred embodiment, it is to be understood that the invention is not limited thereto. It is therefore intended that the following claims be interpreted as covering all such alteration and modifications as fall within the true spirit and scope of the invention.

What is claimed is:

1. An antireflective coating composition, comprising, as a uniform solution in an organic solvent:

an initiator;

a polymerizable oxide-containing colloid, comprising condensation products derived from (i) colloid particles having a formula (I), of Z_xO_y, and (ii) a compound with polymerizable groups having a formula (II), of

$$(R^1)_n\text{—}M(OR^2)_m,$$

wherein

Z is element of Group IIIB, Group IVB, or Group VB, W, Be, Ti, Zr, or Zn;

x and y are integers equal to or more than 1;